2008

Nanodomain Faceting in Ferroelectrics

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Published in *Journal of Physics: Condensed Matter* **20** (2008), 425222 (5 pp); doi 10.1088/0953-8984/20/42/425222

Submitted August 19, 2008; revised September 12, 2008; published September 30, 2008.

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Abstract
We show that after long times (24 h), individual circular domains in 50 nm thick [0 0 1] epitaxial films of ferroelectric lead zirconate titanate (PZT) develop facets due to the crystalline anisotropy, e.g. along [1 0 0] directions. This appears to be a creep process (Tybell et al. 2002 *Phys. Rev. Lett.* **89** 097601; Paruch et al. 2006 *J. Appl. Phys.* **100** 051608) and was first seen in a nanoarray of 180° domains (Ganpule et al. 2002 *Phys. Rev. B* **65** 014101). The effect is independent of polarity and thus rules out any electronic dependence on different work functions for top and bottom electrodes. The phenomenon is interpreted instead as a mechanical relaxation due to highly inhomogeneous stress distributions on the nanodisks, assumed to have stress-free edges.

1. Introduction

The behavior of ferroelectric domains in nanostructures can be different from that of semi-infinite thin films or of bulk specimens [1–11]. However, in all cases the domain reversals occur via switching processes that are inhomogeneous, generally initiated at electrode interfaces, grain boundaries, or other extended defects. Homogeneous nucleation and/or spinodal decomposition are not important processes in these materials. If we examine nucleation on the nanoscale, we find that the process resembles the dynamics of a soap bubble breaking: fluctuations in $+P$ and $-P$ arise and become large; they may shrink and disappear; but like the voids in the surface of a soap bubble, when they reach a critical radius r_0, they grow rapidly. This causes the ferroelectric to switch (or the soap bubble to break). r_0 is typically about 1 nm in a ferroelectric. There is a second, larger, critical size we shall call r_c, below which the surface tension in the newly formed domain makes it circular in the plane parallel to the electrode interface. For domains larger in radius than r_c the crystalline anisotropy dominates the dynamics, and the domain facets along high-symmetry crystallographic axes. r_c is a function of temperature T and of the concentration of extended defects capable of pinning domain walls.

In arrays of 180° domains of epitaxial PZT films Ganpule et al. [12] observed in time-resolved piezoforce microscopy (PFM) the onset of clear faceting at times from $(2.6 \pm 0.2) \times 10^4$ s (i.e., approx. 8 h) to $(2.5 \pm 0.2) \times 10^5$ s (80 h), depending upon voltages, thickness, etc. Exactly when the faceting occurs depends strongly upon defect density; however, the timescale is of order hours or days, not ms or seconds. Defects pin the walls and produce curved 'bowed' walls as the domains expand; the faceting occurs only when the walls break free of the pinning sites. Faceting does not result in stable configurations; re-faceting occurs with time, and each stage must be regarded as only metastable. An important point is that [13] the wall velocity decreases rapidly as the domain radius grows; in fact, the domain wall curvature is a significant part of the driving force for domain expansion. This is very important in the physical understanding of the present experiments, because creep is occurring after the external driving field E is turned off. Thus, it occurs only because of the domain wall curvature. Ganpule et al. estimate a wall energy density U/A of 0.12 J m^{-2} for their PZT domains.

Paruch et al. have shown [14, 15] that the dynamics of PZT domain growth can best be described as creep, with velocity

$$v(E, T) = v_0 \exp\{-\beta(U/kT)[E_0/(E_b + E)]^{\mu}\}. \quad (1)$$

Here the creep exponent μ is 1.0 for creep in a periodic potential but $\mu < 1$ for random potentials. We have added a bias field E_b, due to different top and bottom electrodes, in addition to the applied field E used in [14, 15]. This has the important qualitative effect that v is nonzero in zero applied field (a relaxation velocity). E_b is typically 0.5–1.0 V across 50–200 nm (10 MV m^{-1}) in PZT with dissimilar top and bottom electrodes (Pt/Ir top and $SrRuO_3$ bottom, which have work functions differing by ca 0.6 eV).

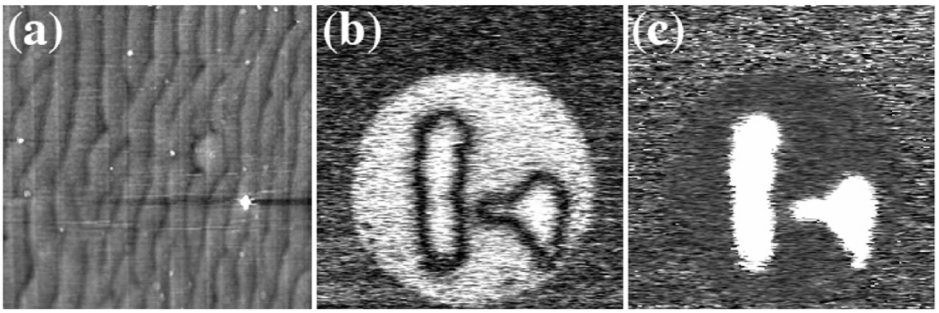

Figure 1. (**a**) Topographic image of the epitaxial lead zirconate titanate (PZT) film used in this work, showing the degree of surface roughness. Scan size is 10 × 10 μm^2. (**b**) PFM amplitude and (**c**) PFM phase images of a circular PZT capacitor partially switched by a voltage pulse of 2.5 V. Scan size is 1.5 × 1.5 μm^2.

Note that the expression in Equation (1) is independent of domain radius r and hence is not a good model for nanodomains, although it is excellent for thin films of larger lateral area. In order to modify it for finite-diameter radii, one would have to include a term corresponding to domain wall surface tension and a term due to crystalline anisotropy. The former term will be isotropic and have v proportional to $1/r$; and the latter will prefer certain axes and vary as some positive power of r.

A semi-empirical extension of Equation (1) is therefore:

$$v(E, T) = v_0(r_0/r) \exp\{-\beta(U/kT)[E_0/(E_b + E)]^{\mu}\} \qquad (2)$$

for the isotropic in-plane wall velocity, with the proviso that the range of validity is for $r > L$, where L is the Larkin length [15]; an additional factor of

$$\Delta v(E, T) = a v_0(r/r_c)^n \qquad (3)$$

should appear in general for an additional anisotropic contribution along specific axes (notably [1 0 0], [0 1 0] or [1 1 1]). n is presumably >1 but unknown (the function is nonlinear but may indeed be exponential or some other non-power-law dependence). No published work yet incorporates such a factor into Equation (2) for an anisotropic theory over all space.

2. Experiment

The present study extends earlier results to the case of circular "vortex" domains in PZT. The topography of the epitaxial film is shown in Figure 1(a) which shows the top surface of a10 × 10 μm^2 surface, with the depth shown as shades of grey or black. Figures 1(b) and (c) show respectively the piezoresponse force microscopy (PFM) amplitude and phase images of a circular 1 μm diameter epitaxial PZT capacitor. As this capacitor contains only antiparallel 180° domains, its PFM phase image consists of black and white regions only, while its PFM amplitude image exhibits dark lines on the bright background representing 180° domain walls.

Figure 2 illustrates the faceting that develops on these initially circular domain patterns after one day at zero field. The original Bessel-function-like domain pattern [16, 17]is now roughly hexagonal.

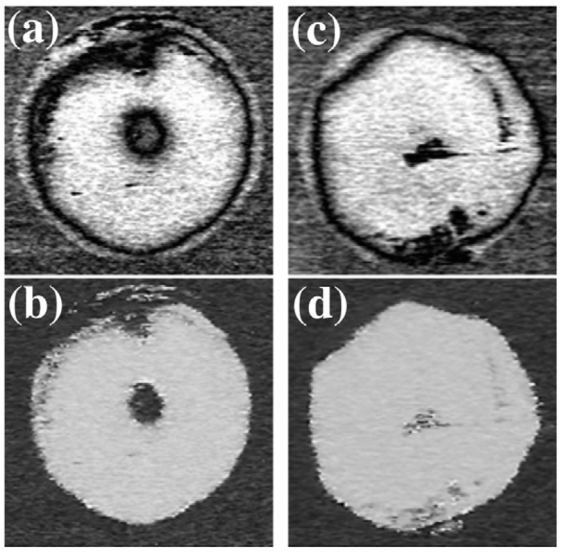

Figure 2. (**a**, **b**) PFM images of domain structure in a PZT capacitor shortly after a 4.5 V pulse of 1 μs duration is applied: (**a**) amplitude and (**b**) phase; (**c**, **d**) PFM images of the same capacitor one day later, showing faceting due to relaxation induced by crystalline anisotropy: (**c**) amplitude and (**d**) phase. Scan size is 1.3 × 1.3 μm^2.

3. Theory

The idea that nanoferroelectrics should develop vortex "closure" domains as in magnets has been put forth very recently theoretically [3–6] and predicted [17] to give polarization patterns that strongly resemble 2nd order Bessel functions. These have been confirmed experimentally [16] and also simulated very accurately with Heisenberg pseudo-spin models [16]. However, no one has yet extended the problem to consider relaxation processes or the effects of crystalline anisotropy. As domains expand which were initially circular, due in part to surface-tension-like stress at the domain walls, the forces keeping them circular decrease with increasing radius and they will eventually become influenced strongly by crystalline anisotropy.

In vortex systems the problem is difficult [18, 19] because of the existence of several critical length scales. However, the length of importance to us is that perpendicular to the direction of polarization P. Moreover, at ambient temperatures

the creep process can be classical, due to thermal hopping, and quantum creep is not required (unlike the case of vortex disclination lines in superconductors [18, 19]).

Therefore we take a simpler approach here: we want to estimate the time required in PZT for the onset of faceting in the relaxing ($E = 0$) state.

3.1. Model of electrically driven domains

The hypothesis that the relaxation is electrically driven is initially plausible because the creep velocities are the right order of magnitude to be explained by the different work functions of top and bottom electrodes:

First we estimate the faceting time from the data in [14] on domain size versus poling time at constant field: by extrapolation of the empirical logarithmic growth data for d = 94 nm epitaxial PZT (within 2× the thickness of our present specimens) during the writing time from Figure 14 of [14], we find $t = 10^4$–10^5 s, in agreement with our observations, under the assumption that the pinning and depinning (poling and depoling) processes take about the same time.

Second, we can try to make an estimate from the dependence of domain size at a constant time upon the applied field: since μ = ca 1.0, we can use the graph of wall velocity versus $1/E$ from [14] to estimate v in Equation (1). Note that in this equation E and v are not necessarily zero, even with no applied voltage, because of the bias voltage in the system (different top and bottom electrodes). For small E ($E \ll 500$ kV cm^{-1}), [14] finds v is nearly constant independent of E, at $v = 10^{-10}$ m s^{-1}. The reason for this plateau in $v(E)$ at small E is not stated, but it might in principle arise from either stress relaxation or bias voltages in the thin films. Thus, to expand to $w = 1$ μm, the time required is $t = w/v = 10^4$ s, in good accord with the present experiments.

However, the observed back-switching behavior is absolutely symmetric if we reverse the polarization from P (up) to P (down). This shows that the back-switching cannot be driven by the different work functions of top and bottom electrodes.

The analysis above is not useless, however, because the creep velocity obtained by Tybell et al. for a small (but unspecified) driving force is ca 10^{-10} ms^{-1}, and hence the domain walls can move ca 1 μm in 24 h, as observed, independent of the nature of the driving force.

3.2. Model of inhomogeneous stress driven (strain gradient driven) domains

It seems more likely to us that the faceting we see in Figure 2 is the result of residual stresses and not due to electrostatics such as the different work functions for top and bottom electrodes. Very recently Gruverman and Oates have reported [20] a finite-element analysis of nanodomain dynamics for doughnut-shaped vortex domains in (1 1 1) PZT. This is a different configuration than that of the (0 0 1) specimens studied in [12]. The mechanism they infer is back-switching under the centers of the top electrodes, which occurs immediately after the applied field is stopped. This is because the mechanical stress is much larger in the 250 nm thick top electrode than in the thin 50 nm deep bottom electrode. The back-switching arises physically because of shear strains imparted on the disk-shaped capacitor, and on the assumption that the edges are stress-free.

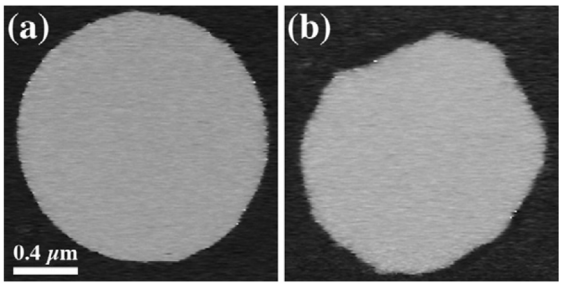

Figure 3. A second experiment showing faceting. Unlike the data in Figure 2, which have approximately hexagonal facets, this figure shows a roughly octagonal polygon.

It is important that the ferroelectric phase transition in PZT is also ferroelastic. This gives rise to certain spatially inhomogeneous effects. Salje has pointed out [21]the following: in case of proper ferroelastic transitions, the elastic constant C_{ij} is the order parameter susceptibility with a lowering of C_{ij} near the ferroelectric transition temperature T_C [22]. In the more common case of an improper ferroelastic transition, no significant softening of C_{ij} occurs near T_C except the dynamical effects described by Carpenter and Salje [23]. All precursor effects described in earlier publications are uniform throughout the sample. The new feature, as described in Salje's paper [21], consists of a heterogeneous precursor. The softer phase nucleates at the surface of the sample as a relaxational deformation. The precursor regions decay exponentially over space [20, 24]. The elastic response of the relaxation region is different from the bulk values but will be difficult to observe in a macroscopic sample unless local indentation or AFM methods are applied [20, 24]. Salje concludes: "in samples with large surface fractions, such as in nanoceramics, these effects should be easily measurable." Although Salje concentrates on phenomena near the phase transition temperature, his analysis shows generally that there will be soft regions in the centers of thin-film nanoferroelectrics, even at temperatures far removed from the Curie temperature. The magnitude of the softening depends upon the electrode-dielectric misfit strain.

The most important prediction of Salje's work is that soft centers will be characteristic of almost all nanostructures, from martensitic metals to ferroelectric ceramics. Combining that with the stress model of back-switching from Gruverman and Oates, we see that a generic description for doughnut-shaped domains exists. This applies peripherally to nanodomain faceting as well, because both are viewed as stress relaxation. Note in Figure 2 that the vertical and horizontal axes are the crystallographic [1 0 0] and [0 1 0] directions. The fact that these align with two of the polygon vertices supports the idea that faceting is due to crystalline anisotropy. However, in Figure 3 this alignment is not so close.

These stress analyses [20, 24] do not readily permit estimates of the times to close "doughnut holes" in domains or to produce faceting. However, they do show that the key

parameter is the misfit strain between electrode and epitaxial film. A check therefore is afforded by varying the electrode metal. In agreement with this interpretation the choice of metal for the top electrode is known to have a large effect on back-switching in PZT [20, 25].

4. Comparison with other faceting studies in nanoferroelectric films

In addition to the seminal work by Ganpule cited above, faceting in micro-crystals of ferroelectric materials have been studied by several other groups: Shur's group in Ekaterinburg has extensively studied $LiNbO_3$ and $LiTaO_3$ [26–28]. Their analyses of faceting—in which they see many regular polygons—is that it is a highly non-equilibrium process involving depolarization screening and back-switching.

Related studies have been carried out by Kalinin et al. [29, 30] by Cho et al. [31], and by Paruch et al. [32]. The work of Kalinin et al. on PZT showed that, as in the present work, the nucleating nanodomains were approximately circular (oblate spheroids in their studies) but faceted with growth; unlike the present study or that of Shur et al., the faceted nanodomains were highly irregular. These authors conclude that the discontinuous jumps in faceting give rise to Barkhausen pulses [29] and that the domain wall profiles are highly dependent upon the film thicknesses [30]. Cho et al. extended the $LiNbO_3$ work to exceptionally small nanodomains (5.1 nm diameter) [31], and made useful arrays of these. Paruch et al. [14, 32] show that the creep exponent decreases dramatically from ca 0.6 to ca 0.2 in epitaxial PZT if it has *a*-axis inclusions. These seem to be dominant pinning sites. A full review is given in [32].

Our observed domains in PZT are larger than those in Paruch's studies: our typical diameter of ca 500 nm is bigger than even the largest domains she wrote with 100–1000 s pulses of 10–12 V. However, her initial studies were done on films grown on Nb:$SrTiO_3$ electrodes. $SrRuO_3$ is a far better metal than the doped semiconducting $SrTiO_3$, but this cannot be the explanation, because her unpublished studies of PZT on $SrRuO_3$ films [33] provide excellent contrast but comparable domain sizes to what she has seen before with the Nb:$SrTiO_3$. We conclude from this comparison that our 50 nm thick epitaxial PZT films (grown at the Max Planck Institute in Halle) have exceptionally low defect concentrations and domain wall pinning rates, a conclusion we reached from other measurements before [16, 34].

Finally, we note that the mechanism of faceting in PZT is unlikely to be the same as in $LiNbO_3$ (or $LiTaO_3$). PZT is strongly ferroelastic (stress–strain hysteresis) whereas $LiNbO_3$ cannot be, since its ferroelectric transition does not change crystal class [35].

As a parenthetical comment, we note that creep and stress relaxation are traditionally not easily modeled by the same approximations: creep cannot be described by the Maxwell model (spring and dashpot in series) which describes exponential stress relaxation very well, whereas creep is well described by the Kelvin–Voigt model (spring and dashpot in parallel) although that model describes relaxation poorly. Thus it is unlikely that any simple model will describe accurately both creep [14, 15] and faceting (relaxation) in nanostructures of PZT.

5. Summary

We report the relaxation of circular vortex domains over a 24 h period in epitaxial [0 0 1] PZT thin films 50 nm thick. We find that the "doughnut" hole in the center vanishes and the circular outer edge forms facets that are usually hexagonal. We interpret these as the long-time relaxation of circular domains that are metastable in part due to surface tension at small times and small (<1 μm) radii but become unstable against the forces of lattice anisotropy with increasing size. The main driving force is the electrode-dielectric lattice mismatch. It has been possible to separate electric effects, such as top electrode work function, from purely elastic relaxation. Further experiments on temperature dependences would be helpful. In addition, changing top electrode metals to vary separately the electrode work functions (electronic) and lattice mismatch onto PZT (mechanical) would quantitatively test the stress driven hypothesis. The idea of surface tension in nanodomains has also been used very recently by Yacoby et al. [36].

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